I. POLYTHIOLESTERS
II. POLYALKYLENE SULFIDES

BY

ALEX KOTCH

B. S., Pennsylvania State College, 1946.
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AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IN CHEMISTRY IN THE GRADUATE COLLEGE
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I. POLYTHIOLESTERS

INTRODUCTION

Extensive investigations have been carried out on polyesters. They became important commercially as alkyd resins and have furnished a wide variety of useful industrial products. The preparation of polyesters has been accomplished by condensation polymerization techniques.

It is surprising that only one investigation (1) has been reported on the sulfur analogs, the polythiolesters. The purpose of this study was to prepare polythiolesters and to compare their physical properties with those of the polyesters. It was demonstrated twelve years ago that a thio acid will add to an unsaturated carbon-carbon double bond in a manner contrary to Markownikoff's rule. However, no work has been reported on the addition of polyfunctional thio acids to polyfunctional olefins. The addition polymerization of dibasic thio acids to diolefins should furnish a convenient route to the formation of polythiolesters, since addition polymerizations are known to produce polymers of very high molecular weight.

Polyalkylene sulfides of very high molecular weight have been prepared in this laboratory by the addition of dithiols to diolefins. Since it was thought that the additive reactivity of a thio acid to a carbon-carbon double bond would be greater than that of a thiol, the addition of dibasic thio acids to diolefins appeared even more attractive.

DISCUSSION

Four new dibasic thio acids have been prepared in fair purity from the corresponding dibasic acid chlorides and hydrogen sulfide in pyridine according to the method of Sunner and Nilson (2). These include dithiolpimelic, dithiolsuberic, dithiolsebacic, and dithiolisophthalic acids. An attempt to prepare dithiolfumaric acid by this method was unsuccessful. The acids in the aliphatic series are very difficult to handle. They have a very unpleasant odor, appear to be hygroscopic, and are readily oxidized and hydrolyzed on exposure to the air.

The following seven polythiolesters have been prepared by the addition of dibasic thio acids to biallyl in benzene solution in quartz flasks by irradiation with ultraviolet light: polyhexamethylene dithioladipate, polyhexamethylene dithiolpimelate, polyhexamethylene dithiolsuberate, polyhexamethylene dithiolazelate, polyhexamethylene dithiolsebacate, polyhexamethylene dithiolterephthalate, polyhexamethylene dithiolisophthalate. The yields ranged from 22 to 92 per cent. The molecular weights of the aliphatic polythiolesters were in the range of 4000-7000, while the molecular weights of the aromatic polymers were about 2000. These polymers are light tan solids and in general melt over a relatively narrow range. They are soluble in benzene, more soluble in chloroform, and insoluble in methanol and water. The polythiolesters are readily hydrolyzed by alcoholic sodium hydroxide but are not hydrolyzed by distilled water in four days at 30°.

The addition of the dibasic thio acids to biallyl was shown to be contrary to Markownikoff's rule, and hence the polymers produced are linear. An X-ray pattern of polyhexamethylene dithioladipate showed very definite evidence of crystallinity. An X-ray pattern of polyhexamethylene dithiolterephthalate showed that this polymer exhibited only small evidence of crystallinity.

Polythiolesters have been made from terephthalyl chloride and four different dithiols in benzene solution in the presence of pyridine. The dithiols used were 1,2-ethanedithiol, tetramethylenedithiol, decamethylenedithiol, and bis (2-mercaptoethyl) sulfide. The yields ranged from 67.7 to 73.5 per cent. Polyethylene dithiolterephthalate melted at 335-340° while the others decreased in melting point as the unit length in the hydrocarbon chain increased. The unit, —$CH_2CH_2SCH_2$-CH_2—, was approximately equivalent to a decamethylene unit in its effect on the melting point. These polymers were insoluble in benzene and only very slightly soluble in hot chloroform. An X-ray pattern of polyethylene dithiolterephthalate showed only slight evidence of crystallinity.

Polythiolesters have been made from adipyl chloride and 1,2-ethanedithiol, tetramethylenedithiol, hexamethylenedithiol, decamethylenedithiol, and bis (2-mercaptoethyl) sulfide. The yields ranged from 47 to 62 per cent, and the approximate molecular weights were in the range 3000-6000. Although the melting points are considerably lower than the corresponding aromatic esters, they illustrate again that an increase in the unit length in the hydrocarbon chain is assocoated with a decrease in the melting point.

An initial attempt to polymerize dithiolterephthalic acid and biallyl in emulsion was unsuccessful.

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II. POLYALKYLENE SULFIDES

INTRODUCTION

In search for polymers which will have desirable properties at low temperatures, different ideas have been advanced concerning the effect of a particular functional group on the physical properties of the polymer. It, therefore, seemed desirable to provide experimental evidence to show the contribution of minor structural changes to the physical properties.

Recently it has been shown (1) that with polyesters and polyurethans the presence of the triple bond is detrimental to polymers which are to be used at low temperatures.

The purpose of this study was to determine the effect of the triple bond in polyalkylene sulfides. To accomplish this it was necessary to prepare polymers of the same size which would have a $—CH_2CH_2—$ unit in one case and in the other a $—C{\equiv}C—$ unit with the remainder of the structure identical. In view of the availabilty of 2-butyne-1,4-diol, a convenient pair of dithiols appeared to be $HSCH_2CH_2CH_2CH_2SH$ and $HSCH_2C{\equiv}CCH_2SH$. If these dithiols were added to the same non-conjugated diolefin, e. g. biallyl, a suitable pair of polymers would be obtained for comparison.

DISCUSSION

Polyalkylene sulfides have been made from tetramethylenedithiol and biallyl in cyclohexane solution under the influence of ultraviolet light. The intrinsic viscosities in benzene were in the range of 0.12 to 0.26. Polyalkylene sulfides of higher molecular weight were made in emulsion using MP-189-EF as the emulsifier and a redox system consisting of ammonium persulfate, sodium bisulfite, and cupric sulfate as initiators. The intrinsic viscosities in benzene were in the range from 0.35 to 0.52. The polymers could be cold-drawn into orientable fibers.

It has been found that an explosion can occur when an impure sample of 2-butyne-1,4-diol is distilled and that 1,4-dichloro-2-butyne is a powerful vesicant.

S-2-Butyne-1,4-diisothiouronium dichloride was prepared from 1,4-dichloro-2-butyne and thiourea in ethanol, and the free base was also isolated. All attempts to hydrolyze either S-2-butyne-1,4-diisothiouronium dichloride or the free base to 2-butyne-1,4-dithiol were unsuccessful even in a nitrogen atmosphere and in the presence of inhibitors.

A condensation technique was developed for preparing polyalkylene sulfides of high molecular weight from dihalides and dimercaptides. A polymer having an intrinsic viscosity of 0.63 was prepared from tetramethylene dibromide and the disodium dimercaptide of hexamethylenedithiol.

Application of the new condensation polymerization technique to the preparation of a polyalkylene sulfide from 1,4-dichloro-2-butyne and hexamethylenedithiol failed to produce a solid polymer at 80° or at room temperature.

No reaction occurred between 1,4-dichloro-2-butyne and hexamethylenedithiol when they were stirred with a suspension of calcium carbonate in benzene.

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VITA

The author was born in Edwardsville, Pennsylvania, on August 18, 1926. After attending high school there, he entered Bucknell Junior College (now Wilkes College) in Wilkes-Barre, Pennsylvania, in February, 1943, and was graduated in June, 1944. He entered the Pennsylvania State College, State College, Pennsylvania, in October, 1944, was recipient twice of the Class of 1922 Memorial Scholarship, was named an Evan Pugh Scholar, and was named salutatorian of the graduating class in June, 1946, when he received the degree of Bachelor of Science in Chemistry. He held a half-time teaching assistantship in organic chemistry at Penn State from July, 1946, until August, 1947, at which time he received the degree of Master of Science in Chemistry. In October, 1947, he entered the graduate school of the University of Illinois and held a half-time teaching assistantship in organic chemistry from October, 1947, until June, 1949. During the summer of 1949 he was employed at the Hercules Powder Company in Wilmington, Delaware. During the school year, 1949-1950, he held the Monsanto Chemical Company Fellowship.